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(54) [Title of the Invention] **CURABLE RESIN COMPOSITIONS**

(57) [Abstract]

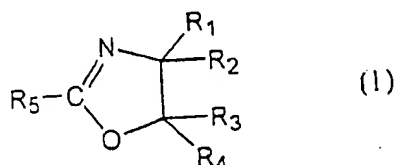
[Object] To provide curable resin compositions that show excellent storage stability, solvent resistance, reagent resistance, water resistance, blocking resistance, hardness and especially excellent weather resistance over a long period of time and that can cause curing to occur at a low temperature and can give a coated film with excellent external appearance and smoothness.

[Means for Accomplishing Object] The necessary component of the composition is the vinyl type polymer (P) that can be obtained by polymerizing the polymerizable monomer component (p). This polymerizable monomer component consists of at least 5.0-99.99 wt. % of the polymerizable monomer (a) containing more than one kind of monomer selected from the group consisting of the polymerizable monomers having an epoxy group (a1) and the polymerizable monomers having an oxazoline group with a specific structure (a2) and 0.01-20.0 wt. % of the polymerizable monomer (b) with a specific structure known as an ultraviolet light absorbing agent or an ultraviolet light stabilizer (but the sum of the wt. % of each monomer making up the polymerizable monomer component (p) is set to be 100 wt. %).

[Scope of the Patent Claims]

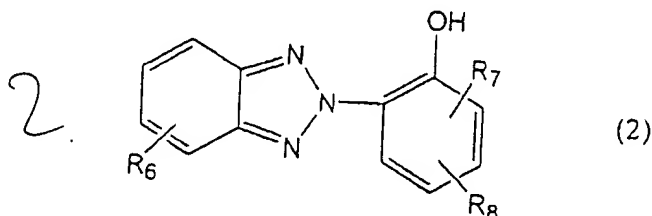
[Claim 1] Curable resin compositions containing a vinyl type polymer (P) as their necessary component, which vinyl type polymer can be obtained by polymerizing the polymerizable monomer component (p) containing 5.0-99.99 wt. % of more than one kind of the polymerizable monomers (a) selected from the group consisting of the polymerizable monomers having an epoxy group (a1) and the polymerizable monomers having an oxazoline group that can be represented by the general formula (1) given below (a2) and 0.01-20.0 wt. % of at least one kind of the polymerizable monomers (b) selected from the group consisting of the polymerizable monomers that can be represented by the general formula (2) given below (b1), the polymerizable monomers that can be represented by the general formula (3) given below (b2) and the polymerizable monomers that can be represented by the general formula (4) given below (b3) (but the sum of the wt. % of each monomer making up the polymerizable monomer component (p) is set to be 100 wt. %).

[Chemical Formula 1]



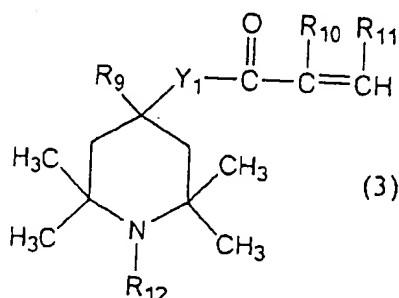
(in which R₁, R₂, R₃ and R₄ each independently denote a hydrogen atom, a halogen group, an alkyl group, an aralkyl group, a cycloalkyl group, an aryl group or a substituted aryl group; R₅ denotes an alkenyl group or a cycloalkenyl group)

[Chemical Formula 2]



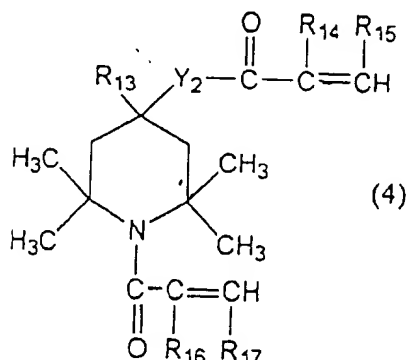
(in which R₆, R₇ and R₈ each independently denote a substituting group; among R₆, R₇ and R₈, at least one of them represents an organic group having an unsaturated double bond and the other groups denote an alkyl group, an alkenyl group, an aralkyl group, an aryl group, an alkoxy group, an aralkoxy group, a hydroxyl group, a halogen group, a sulfonic acid (ester) group, a carboxylic acid (ester) group or a phosphoric acid (ester) group).

[Chemical Formula 3]



(in which R_9 denotes a hydrogen atom or a cyano group and R_{10} and R_{11} each independently denote a hydrogen atom or a hydrocarbon group having 1-2 carbon atoms; R_{12} denotes a hydrogen atom or a hydrocarbon group having the number of carbon atoms in the range of 1-18; Y_1 denotes an oxygen atom or an imino group).

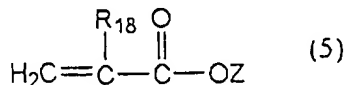
[Chemical Formula 4]



20 (in which R_{13} denotes a hydrogen atom or a cyano group; R_{14} , R_{15} , R_{16} and R_{17} each independently denotes a hydrogen atom or a hydrocarbon group having 1-2 carbon atoms and Y_2 denotes an oxygen atom or an imino group).

[Claim 2] Curable resin compositions in accordance with claim 1, in which the said polymerizable monomer component (p) contains, in addition to the said polymerizable monomer (a) and the said polymerizable monomer (b), the polymerizable monomer (c) that can be represented by the general formula (5) given below.

[Chemical Formula 5]



(in which R_{18} denotes a hydrogen atom or a methyl group and Z denotes a hydrocarbon group having more than 4 carbon atoms).

40 [Claim 3] Curable resin compositions in accordance with claim 1 or 2 that contain, in addition to the said vinyl type polymer (P), a crosslinking agent (Q) made of a compound having more than two acid groups in its molecule.

[Claim 4] Curable resin compositions in accordance with claim 3, in which the said crosslinking agent (Q) is a polycarboxylic acid.

[Claim 5] Curable resin compositions in accordance with claim 3 or 4, in which the amount of the acid groups of the said crosslinking agent (Q) is 5-1.5 equivalents with respect to 1 equivalent of the epoxy group and the oxazoline group of the said polymerizable monomer (a).

[Detailed Description of the Invention]

50 [0001]

[Field of Industrial Application] The present invention pertains to a curable resin composition that can undergo curing at a low temperature in a short period of time.

[0002]

[Prior Art] The curable resin compositions that utilize the reaction between an epoxy group or an oxazoline group and a compound having a functional group capable of reacting with the said functional groups in its molecule show such advantageous characteristics as curability, reagent resistance, solvent resistance, water resistance, etc., and thus are widely used in the fields of paints, surface treating agents, coating agents, bonding agents, adhesives, sealing agents, forming materials, etc. E.g., a heat-curable solvent type resin composition consisting of an acryl copolymer having epoxy groups and an acryl copolymer having acid groups has been described in Patent
 10 Disclosure No. Hei 1-[1989]-139,653, a heat-curable resin composition for use in a powder paint consisting of a polymer containing an acrylic acid (or methacrylic acid) ester having a glycidyl group and an aliphatic dibasic acid has been described in Patent Disclosure No. Sho 50-[1975]-124,934 and a curable resin composition consisting of a compound having an oxazoline group and a compound having a carboxyl group has been described in Patent Disclosure No. Hei 5-[1993]-25,361.

[0003] For curing these prior-art curable resin compositions, a curing temperature in the range of 140-180°C and a curing time of about 30 minutes are needed. From the standpoints of productivity and energy savings, it is desirable to develop a curable resin composition that can be cured at a lower temperature in a shorter period of time. In general, however, when a curable resin composition is cured at a low temperature or in a short time,
 20 decreases in its ability to provide weather resistance, solvent resistance, reagent resistance, water resistance, blocking resistance, hardness, etc. and also in its ability to provide excellent external appearance and smoothness, etc. of the coated film will occur easily. In addition, in order for a curable resin composition to cure at a low temperature or in a short time, addition of a curing catalyst for promoting the curing reaction has been proposed, but the addition of the curing catalyst to the curable resin composition will lower the storage stability and the weather resistance of the composition.

[0004]

[Object of the Invention] Therefore, the task of the present invention was to develop curable resin compositions with especially excellent long-term weather resistance and excellent storage stability that can be cured at a low
 30 temperature in a short period of time and that can provide solvent resistance, reagent resistance, water resistance, blocking resistance, hardness and excellent external appearance and smoothness of the coated film.

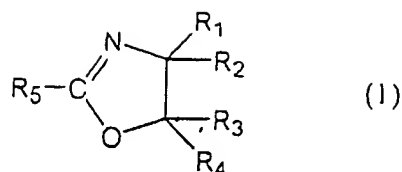
[0005]

[Means for Accomplishing the Object] We carried out extensive studies in order to accomplish the object mentioned above and found that a specific structure in a polymerizable monomer known as an ultraviolet light absorbing agent or ultraviolet light stabilizer showed not only the ability to absorb ultraviolet light and ultraviolet light stabilization but also the ability to serve as a curing catalyst. We also discovered that by allowing a curable
 40 resin composition to contain a vinyl type polymer copolymerized with the said polymerizable monomer, the resin composition would become curable at a low temperature in a short time without adversely affecting its storage stability and weather resistance. These findings led us to develop the present invention.

[0006] Namely, the curable resin compositions of the present invention contain the curable resin compositions with the vinyl type polymer (P) as their necessary component, which vinyl type polymer can be obtained by polymerizing the polymerizable monomer component (p) containing 5.0-99.99 wt. % of more than one kind of the polymerizable monomers (a) selected from the group consisting of the polymerizable monomers having an epoxy group (a1) and the polymerizable monomers having an oxazoline group that can be represented by the general formula (1) given below (a2) and 0.01-20.0 wt. % of at least one kind of the polymerizable monomers (b) selected
 50 from the group consisting of the polymerizable monomers that can be represented by the general formula (2) given below (b1), the polymerizable monomers that can be represented by the general formula (3) given below (b2) and the polymerizable monomers that can be represented by the general formula (4) given below (b3) (but the sum of the wt. % of each monomer making up the polymerizable monomer component (p) is set to be 100 wt. %).

[0007]

[Chemical Formula 6]

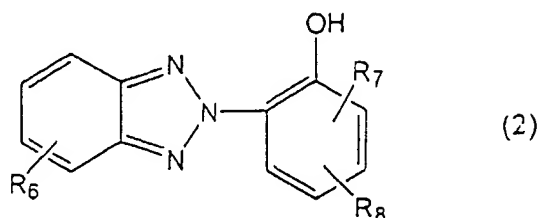


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[0008] (in which R_1 , R_2 , R_3 and R_4 each independently denote a hydrogen atom, a halogen group, an alkyl group, an aralkyl group, a cycloalkyl group, an aryl group or a substituted aryl group; R_5 denotes an alkenyl group or a cycloalkenyl group)

[0009]

[Chemical Formula 7]



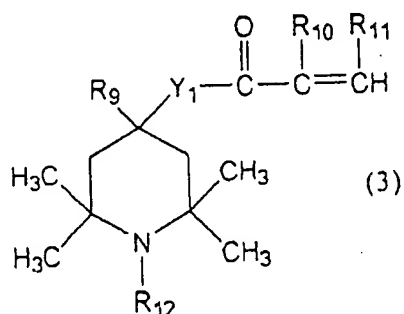
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[0010] (in which R_6 , R_7 and R_8 each independently denote a substituting group; among R_6 , R_7 and R_8 , at least one of them represents an organic group having an unsaturated double bond and the other groups denote an alkyl group, an alkenyl group, an aralkyl group, an aryl group, an alkoxy group, an aralkoxy group, a hydroxyl group, a halogen atom, a sulfonic acid (ester) group, a carboxylic acid (ester) group or a phosphoric acid (ester) group).

30

[0011]

[Chemical Formula 8]



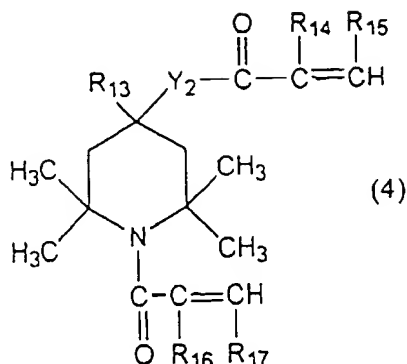
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[0012] (in which R_9 denotes a hydrogen atom or a cyano group and R_{10} and R_{11} each independently denote a hydrogen atom or a hydrocarbon group having 1-2 carbon atoms; R_{12} denotes a hydrogen atom or a hydrocarbon group having the number of carbon atoms in the range of 1-18; Y_1 denotes an oxygen atom or an imino group).

50

[0013]

[Chemical Formula 9]



20 [0014] (in which R_{13} denotes a hydrogen atom or a cyano group; R_{14} , R_{15} , R_{16} and R_{17} each independently denotes a hydrogen atom or a hydrocarbon group having 1-2 carbon atoms and Y_2 denotes an oxygen atom or an imino group).

[0015]

30 [Embodiment of Implementation of the Invention] One embodiment of implementation of the present invention is explained in detail below. The curable resin compositions of the present invention contain the vinyl type polymer (P) as their essential component and the polymerizable monomer component (p) making up the vinyl type polymer (P) contains at least one polymerizable monomer (a) selected from the group consisting of the polymerizable monomers having an epoxy group (a1) and the polymerizable monomer having an oxazoline group (a2). By allowing the vinyl type polymer (P) to contain the polymerizable monomer (a) mentioned above, crosslinking points can be created in the vinyl type polymer (P) and hence excellent mechanical characteristics such as hardness, flexibility, etc. can be obtained after the curable resin composition has been cured.

40 [0016] There is no specific restriction as to the polymerizable monomer having an epoxy group (a1) as long as it is a compound having an epoxy group and an unsaturated double bond. Specifically, they include, e.g., glycidyl esters of acrylic or methacrylic acid such as glycidyl acrylate or methacrylate, β -methyl glycidyl acrylate or methacrylate, etc.; allyl glycidyl ethers such as allyl glycidyl ether, allyl methyl glycidyl ether, etc.; vinyl type monomers containing an alicyclic type epoxy group such as 3,4-epoxy cyclohexyl acrylate, 3,4-epoxy cyclohexyl methacrylate, etc. These compounds can be used individually or in combination of more than two kinds.

[0017] The polymerizable monomer having an oxazoline group (a2) is a compound that can be represented by the said formula (1). Specific examples of the polymerizable monomers having an oxazoline group (a2) are, e.g., 2-vinyl-2-oxazoline, 2-vinyl-4-methyl-2-oxazoline, 2-vinyl-5-methyl-2-oxazoline, 2-isopropenyl-2-oxazoline, 2-isopropenyl-4-methyl-2-oxazoline, 2-isopropenyl-5-methyl-2-oxazoline, 2-isopropenyl-5-ethyl-2-oxazoline, etc. They can be used individually or in combination of more than two kinds.

50 [0018] The content of the said polymerizable monomer (a) in the polymerizable monomer component (p) should be in the range of 5.0-99.99 wt. % or preferably 10.0-70.0 wt. % or more preferably 15.0-40.0 wt. %. When the content of the polymerizable monomer (a) is less than 5 wt. %, the crosslinking density will decrease and water resistance, solvent resistance, such reagent resistance as acid resistance, alkali resistance, etc., and hardness will decrease. In contrast, when the content is greater than 99.99 wt. %, the content of the subsequent polymerizable monomer (b) will decrease and sufficient low temperature curability and improved weather resistance cannot be expected. Moreover, the polymerizable monomer component (p) may contain either the polymerizable monomer having an epoxy group (a1) or the polymerizable monomer having an oxazoline group (a2) or may contain both of them but the content of the sum of (a1) and (a2) should be within in the range mentioned above.

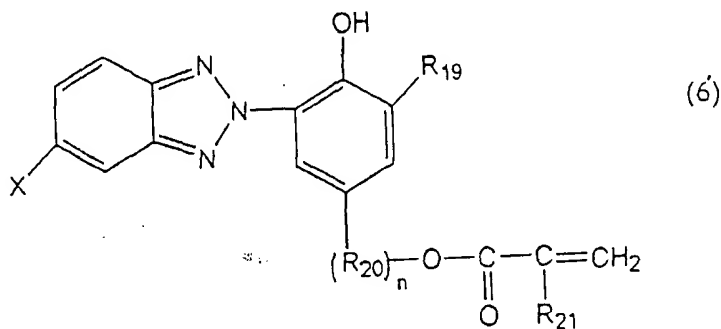
[0019] The said polymerizable monomer component (p) of the present invention contains at least one of the polymerizable monomers (b) selected from the group consisting of the polymerizable monomers (b1) that can be represented by the said formula (2), the polymerizable monomers (b2) that can be represented by the said formula (3) and the polymerizable monomers (b3) that can be represented by the said formula (4). The polymerizable monomers (b) with a specific structure will act as a curing catalyst to improve the curing characteristics.

Therefore, by allowing a curable resin composition to contain the polymerizable monomers (b), curing at a low temperature in a short period of time will become possible. Especially, the polymerizable monomer (b2) and the polymerizable monomer (b3) can act effectively and favorably on the low temperature curability and thus are preferable. Moreover, the polymerizable monomer (b1) can also act as an ultraviolet light absorbing monomer and will exert its effect after being incorporated into the polymer (P) and thus weather resistance, especially long-term weather resistance, can be improved.

[0020] The polymerizable monomer (b1) is a benzotriazole type ultraviolet light absorbing monomer that can be represented by the said general formula (2). Specifically, the compounds that can be represented by the said general formula (2) include the compounds that can be represented by the general formula (6) given below,

[0021]

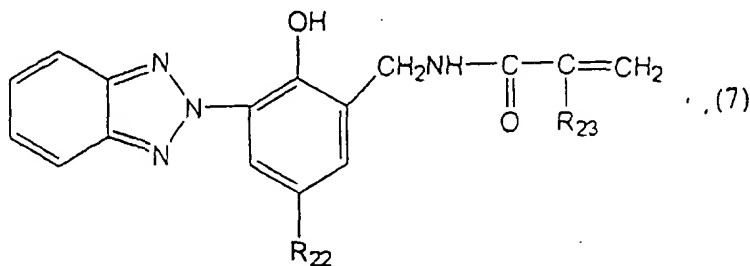
[Chemical Formula 10]



[0022] (in which X denotes a hydrogen atom or a chlorine atom; R_{19} denotes a hydrogen atom, a methyl group or a tertiary alkyl group with the number of carbon atoms in the range of 4-8; R_{20} denotes a straight chain or a branched chain alkylene group with the number of carbon atoms in the range of 1-10; R_{21} denotes a hydrogen atom or a methyl group; n denotes 0 or 1), the compounds that can be represented by the general formula (7) given below,

[0023]

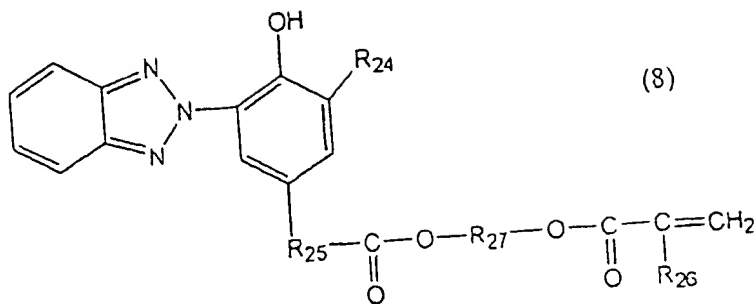
[Chemical Formula 11]



[0024] (in which R_{22} is the same as R_{19} in the said general formula (6) and R_{23} is the same as R_{21} in the said general formula (6)), and the compounds that can be represented by the general formula (8) given below.

[0025]

[Chemical Formula 25]



[0026] (in which R_{24} is the same as R_{19} in the said general formula (6), R_{25} is the same as R_{20} in the said general formula (6), R_{26} is the same as R_{21} in the said general formula (6) and R_{27} denotes a $-C_2H_4-$ group or a $-CH_2CH(OH)CH_2-$ group). The tertiary alkyl groups with the number of carbon atoms in the range of 4-8 that are represented by R_{19} , R_{22} and R_{24} in the said general formulas (6)-(8) include, e.g., a *tert.*-butyl group, a *tert.*-pentyl group, a *tert.*-hexyl group, a *tert.*-heptyl group, a *tert.*-octyl group, a di-*tert.*-octyl group, etc. The straight chain or branched chain alkylene groups with the number of carbon atoms in the range of 1-10 that are represented by R_{20} and R_{25} in the said general formulas (6) and (8) include, e.g., an ethylene group, a trimethylene group, a propylene group, a tetramethylene group, a 1,1-dimethyltetramethylene group, a butylene group, an octamethylene group, an octylene group, a decamethylene group, a decylene group, etc. Among these groups, the ethylene group and propylene group are preferable.

[0027] Specific examples of the compounds that can be represented by the said general formula (6) are, e.g., 2-[2'-hydroxy-3'-*tert.*-butyl-5'-(methacryloyloxymethyl)phenyl]-2H-benzotriazole, 2-[2'-hydroxy-5'-(methacryloyloxyethyl)phenyl]-2H-benzotriazole, 2-(2'-hydroxy-5'-(methacryloyloxypropyl)phenyl)-2H-benzotriazole, 2-(2'-hydroxy-5'-methacryloyloxypropyl-3'-*tert.*-butylphenyl)-5-chloro-2H-benzotriazole, 2-[2'-hydroxy-5'-(acryloyloxymethyl)phenyl]-2H-benzotriazole, 2-[2'-hydroxy-3'-*tert.*-butyl-5'-(methacryloyloxyethyl)phenyl]-5-chloro-2H-benzotriazole, 2-[2'-hydroxy-3'-methyl-5'-(acryloyloxyoctyl)phenyl]-2H-benzotriazole, etc.

[0028] Specific examples of the compounds that can be represented by the said general formula (7) include, e.g., 2-[2'-hydroxy-5'-*tert.*-butyl-3'-(methacrylamidomethyl)phenyl]-2H-benzotriazole, 2-[2'-hydroxy-5'-*tert.*-octyl-3'-(methacrylamidomethyl)phenyl]-2H-benzotriazole, etc.

[0029] Specific examples of the compounds that can be represented by the said general formula (8) include, e.g., 2-[2'-hydroxy-3'-*tert.*-butyl-5'-2-(2-methacryloyloxyethoxycarbonyl)ethylphenyl]-2H-benzotriazole, 2-[2'-hydroxy-3'-*tert.*-butyl-5'-2-(3-methacryloyloxy-2-hydroxypropoxycarbonyl)ethylphenyl]-2H-benzotriazole, etc.

[0030] The polymerizable monomers (b1) that can be represented by the said general formula (2), also include, e.g., in addition to the compounds that can be represented by the general formulas (6)-(8), benzotriazole type ultraviolet light absorbing monomers such as 2-[2'-hydroxy-5'-(β -methacryloyloxyethoxy)-3'-*tert.*-butylphenyl]-4'-*tert.*-butyl-2H-benzotriazole, etc.

[0031] Among the compounds listed above, the compounds that can be represented by the general formula (6) are especially suitable for use as the polymerizable monomer (b1). The compounds listed above can be used individually or in combination of more than two kinds. The polymerizable monomer (b2) is a piperidine type compound that can be represented by the said general formula (3), in which the hydrocarbon groups with the number of carbon atoms in the range of 1-18 that are represented by R_{12} include, e.g., a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, an isobutyl group, a *tert.*-butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group, a

tridecyl group, a tetradecyl group, a pentadecyl group, a hexadecyl group, a heptadecyl group, an octadecyl group, etc.

[0032] Specifically, the polymerizable monomers (b2) that can be represented by the said general formula (3) include, e.g., 4-acryloyl or methacryloyloxy-2,2,6,6-tetramethylpiperidine, 4-acryloyl or methacryloylamino-2,2,6,6-tetramethylpiperidine, 4-acryloyl or methacryloyloxy-2,2,6,6-tetramethylpiperidine, 4-acryloyl or methacryloyloxy-1,2,2,6,6-pentamethylpiperidine, 4-acryloyl or methacryloylamino-1,2,2,6,6-pentamethylpiperidine, 4-cyano-4-acryloyl or methacryloylamino-2,2,6,6-tetramethylpiperidine, 4-crotonoyloxy-2,2,6,6-tetramethylpiperidine, 4-crotonoylamino-2,2,6,6-tetramethylpiperidine, etc. They may be used individually or in combination of more than two kinds.

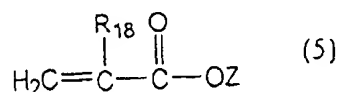
[0033] The polymerizable monomers (b3) are piperidine type compounds that can be represented by the said general formula (4). Specifically, they include, e.g., 1-acryloyl or methacryloyl-4-acryloyl or methacryloylamino-2,2,6,6-tetramethylpiperidine, 1-acryloyl or methacryloyl-4-cyano-4-acryloyl or methacryloylamino-2,2,6,6-tetramethylpiperidine, 1-crotonoyl-4-crotonoyloxy-2,2,6,6-tetramethylpiperidine, etc. They may be used individually or in combination of more than two kinds.

[0034] The polymerizable monomers (b) include at least one monomer selected from the group consisting of the polymerizable monomers (b1), (b2) and (b3). A mixture of more than two kinds may also be used. The content of the said polymerizable monomer (b) in the polymerizable monomer component (p) should be in the range of 0.01-20.0 wt. % or preferably 0.05-15.0 wt. % or more preferably 0.1-10.0 wt. %. When the content of the polymerizable monomer (b) is less than 0.01 wt. %, sufficient improvement in low temperature curability and weather resistance cannot be achieved. In contrast, when the content is greater than 20.0 wt. %, water resistance and storage stability will decrease and the external appearance of the coated film will tend to be poor. When more than two kinds of monomers are selected from (b1) to (b3) as the polymerizable monomer (b), the total amount of sum of these monomers in the polymerizable monomer (b) should be within the range mentioned above.

[0035] In addition to the polymerizable monomer (a) and the polymerizable monomer (b), it is desirable from the standpoint of weather resistance that the polymerizable monomer component (p) contain the polymerizable monomers (c) that can be represented by the general formula (5) given below.

[0036]

[Chemical Formula 13]



[0037] (in which R_{18} denotes a hydrogen atom or a methyl group and Z denotes a hydrocarbon group with the number of carbon atoms greater than 4). In the said general formula (5), the hydrocarbon groups with the number of carbon atoms greater than 4 that are represented by Z include, e.g., alicyclic hydrocarbon groups such as a cyclohexyl group, a methyl cyclohexyl group, a cyclododecyl group, etc.; straight chain or branched chain alkyl groups such as a butyl group, an isobutyl group, a *tert.*-butyl group, a 2-ethylhexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group, a pentadecyl group, an octadecyl group, etc.; polycyclic hydrocarbons such as a bornyl group, an isobornyl group, etc. Among these compounds, the alicyclic hydrocarbon groups, branched chain alkyl groups and straight chain alkyl groups with the number of carbon atoms greater than 6 are especially preferable.

[0038] Specific examples of the polymerizable monomers (c) that can be represented by the said general formula (5) include, e.g., cyclohexyl acrylate or methacrylate, methyl cyclohexyl acrylate or methacrylate, cyclododecyl acrylate or methacrylate, *tert.*-butylcyclohexyl acrylate or methacrylate, isobutyl acrylate or methacrylate, *tert.*-butyl acrylate or methacrylate, lauryl acrylate or methacrylate, isobornyl acrylate or methacrylate, stearyl acrylate or methacrylate, 2-ethyl hexyl acrylate or methacrylate, *n*-butyl acrylate or methacrylate, tridecyl acrylate or methacrylate. Among these compounds, cyclohexyl acrylate or methacrylate is especially suitable because it can provide excellent hardness, weather resistance and resistance against such reagents as acids, alkali, etc.

[0039] When the polymerizable monomer component (p) contains the said polymerizable monomer (c), it is desirable that its content in the polymerizable monomer component (p) is 5.0-70.0 wt. % or preferably 10.0-50.0 wt. % or more preferably 20-50 wt. %. When the content of the polymerizable monomer (c) is less than 50.0 wt. %, sufficient improvement in weather resistance cannot be expected. In contrast, when the content is greater than 70 wt. %, the solvent resistance tends to decrease. Therefore, contents less than 5 wt. % or greater than 70.0 wt. % are not desirable.

[0040] In addition to the said polymerizable monomer (a), the said polymerizable monomer (b) and the polymerizable monomer (c), the polymerizable monomer component (p) of the present invention may also contain other polymerizable monomers that can copolymerize with the said monomers. By allowing the polymerizable monomer component (p) to contain these other polymerizable polymers, the curable resin composition can be adjusted to have a proper balance of physical properties.

[0041] These other copolymerizable polymerizable monomers include, e.g., mono- or diesters formed between monomers that contain acrylic or methacrylic acid, crotonic acid, such polycarboxylic acids as itaconic acid, maleic acid, fumaric acid, etc., and monoalkyl alcohols having the number of carbon atoms in the range of 1-18. Specific examples of such monomers include, e.g., acrylates or methacrylates that can be synthesized by esterification of acrylic acid or methacrylic acid with alcohols having 1-3 carbon atoms such as methyl acrylate or methacrylate, ethyl acrylate or methacrylate, etc.; acrylate or methacrylate having a hydroxyl group such as 2-hydroxyethyl acrylate or methacrylate, 2-hydroxypropyl acrylate or methacrylate, 4-hydroxybutyl acrylate or methacrylate, monoesters of acrylic acid or methacrylic acid and polypropylene glycol or polyethylene glycol, caprolactone modified hydroxy acrylate or methacrylate (e.g., "Plackcell FM", a brand name, manufactured by Daicell Co. Ltd.), etc.; acrylates or methacrylates having an amino acid such as *tert*.-butylaminoethyl acrylate or methacrylate, *tert*.-butylaminopropyl acrylate or methacrylate, pyrrolidinyl ethyl acrylate or methacrylate, piperidinyl acrylate or methacrylate, etc.; multifunctional acrylates or methacrylates having more than 2 polymerizable unsaturated groups in their molecules such as esters of acrylic acid or methacrylic acid and such polyhydric alcohols as ethylene glycol, 1,3-butylene glycol, diethylene glycol, 1,6-hexane glycol, neopentyl glycol, polyethylene glycol, polypropylene glycol, trimethylol propane, pentaerythritol, dipentaerythritol, etc.

[0042] also, such olefins as ethylene, propylene, *n*-butene, etc.; halogenated olefins excluding fluoro olefins such as vinyl chloride, vinylidene chloride, etc.; fluorine containing olefins such as vinyl fluoride, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene, chlorotrifluoroethylene, bromotrifluoroethylene, pentafluoropropylene, hexafluoropropylene, etc.; styrene derivatives such as styrene, vinyl toluene, α -methyl styrene, chloromethyl styrene, styrene sulfonic acid and its salts, etc.; vinyl esters such as vinyl acetate, vinyl propionate, vinyl stearate, vinyl butyrate, vinyl isobutylate, vinyl caproate, vinyl caprylate, vinyl caprate, vinyl laurate, vinyl branched chain aliphatic carboxylates with number of carbon atoms in the range of 9-11, etc.; vinyl esters of carboxylic acids having a cyclic structure such as vinyl cyclohexane carboxylate, vinyl methyl cyclohexane carboxylate, vinyl benzoate, vinyl *p*-*tert*.-butyl benzoate, etc.; vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, octyl vinyl ether, lauryl vinyl ether, etc.; fluorovinyl monomers, e.g., such perfluoroalkylperfluorovinyl ethers or (per)fluoroalkylvinyl ethers (but, the number of carbon atoms in the alkyl group is in the range of 1-18) such as trifluoromethylfluorovinyl ether, pentafluoroethyltrifluorovinyl ether, heptafluoropropyltrifluorovinyl ether, etc.; acryl or methacryl amides such as acryl or methacryl amide, *N*-monomethylacryl or methacrylamide, *N*-monoethylacryl or methacrylamide, *N,N*-dimethylacryl or methacrylamide, *N*-methylolacryl or methacrylamide, *N*-butoxyacryl or methacrylamide, *N*-dimethylaminoethylacryl or methacrylamide, *N*-diethylaminopropylacryl or methacrylamide, *N*-diethylaminopropylacryl or methacrylamide, etc.; basic unsaturated monomers such as dimethylaminoethyl acrylate or methacrylate, diethylaminoethyl acrylate or methacrylate, dimethylaminoethyl acryl or methacryl amide, dimethylaminopropylacryl or methacrylamide, vinyl pyridine, vinyl imidazole, vinyl pyrrolidone, etc.; unsaturated sulfonic acids such as 2-sulfonic acid ethyl acrylate or methacrylate and their salts, vinyl sulfonic acid and its salts, etc.; modified caprolactone compounds of acrylic or methacrylic acid; acrylo- or methacrylonitrile; unsaturated monomers containing an organic silicon such as vinyl trimethoxy silane, γ -acryloyl or methacryloyloxypropyl trimethoxy silane, γ -acryloyl or methacryloyloxypropyl triethoxy silane, γ -acryloyl or methacryloyloxypropyl methyltrimethoxy silane, allyl triethoxy silane, trimethoxy silyl propyl allyl amine, etc. They can be used individually or a properly mixed mixture of more than two of these compounds may be used.

[0043] There is no specific restriction as to the amount of the said other polymerizable monomers used as the polymerizable monomer component (p), but it is desirable that the amount used is less than 94.99 wt. % or

preferably in the range of 15.0-89.95 wt. % or more preferably 50-84.9 wt. %. However, the total wt. % of all of the said monomers in the polymerizable monomer component (p) should be adjusted to be 100 wt. %.

[0044] The vinyl type polymer (P) can be obtained by polymerizing the said polymerizable monomer component (p) with the use of a well-known radical polymerization procedure. There is no specific restriction as to the polymerization procedure that can be used; e.g., a solution polymerization procedure, a suspension polymerization procedure, a block polymerization procedure, an emulsion polymerization procedure, etc., may be used. The polymerization process for obtaining the vinyl type polymer (P) can be carried out with or without using a solvent. When a solvent is used, there is no specific restriction as to the kind or the amount of the solvent used; namely any properly selected solvent can be used. Specific examples of such solvents include, e.g., aromatic hydrocarbons such as toluene, xylene, etc.; acetic acid esters such as ethyl acetate, butyl acetate, isobutyl acetate, etc.; ketones such as methyl ethyl ketone, etc.; ethers of alkylene glycols such as propylene glycol monomethyl ether acetate, dipropylene glycol monomethyl ether acetate, diethylene glycol monomethyl ether acetate, etc.; alcohols such as methyl alcohol, *n*-butyl alcohol, *tert*.-butyl alcohol, isopropyl alcohol, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, ethylene glycol, etc. They can be used individually or as a solvent mixture. Moreover, all or part of these solvents may be removed by distillation after the polymerization process.

[0045] If necessary, a polymerization initiating agent can be used in the synthesis of the vinyl type polymer (P). There is no specific restriction as to the polymerization initiating agents that can be used in the present invention. They include, e.g., such general radical polymerization initiating agents as azo type compounds such as azobisisobutyronitrile, azobis(2-methyl)butyronitrile, etc.; peroxide type compounds such as benzoyl peroxide, di(*tert*.-butyl)peroxide, etc. There is no specific restriction as to the amount of such initiating agents used but it is preferable that the amount used is in the range of 0.1-10 wt. % with respect to the total amount of the monomer used.

[0046] There is no specific restriction as to the reaction temperature used in the polymerization reaction for obtaining the vinyl type polymer (P) but it is preferable that the temperature is in the range of room temperature to 200°C or preferably 40-150°C. Moreover, if necessary, a surface active agent, a chain transfer agent, a chain adjusting agent, etc., may be used during the process of obtaining the vinyl type polymer (P). It is desirable that the average molecular weight of the vinyl type polymer (P) is in the range of 1,000-50,000, or preferably 1,500-30,000 or more preferably 2,000-10,000. It is especially desirable that the amount of the component with molecular weight less than 1,000 is less than 10 wt. %. The number average molecular weight less than 1,000 is not desirable because it will be difficult to obtain sufficient durability. On the other hand, the number average molecular weight greater than 50,000 is not desirable because the polymerization stability will decrease and the viscosity will become high, reducing the workability.

[0047] It is desirable that the glass transition temperature (T_g) of the vinyl type polymer (P) is in the range of 0-100°C or preferably 15-85°C or more preferably 30-70°C. When T_g is below 0°C, the hardness will decrease, excessive softness will appear and the durability tends to decrease. In contrast, when it is higher than 100°C, brittleness will appear and cracks will form easily. Moreover, T_g is measured with the use of a differential scanning calorimeter (DSC).

[0048] A cationic polymerization catalyst may be added to the said vinyl type polymer (P). There is no specific restriction as to the cationic polymerization catalyst that can be used. Specifically, they include, e.g., such latent cationic polymerization catalysts as sulfonium salts such as benzyl-4-hydroxyphenylmethyl sulfonium hexafluoroantimonate, triphenylsulfonium boron tetrafluoride, triphenylsulfonium antimony hexafluoride, *p*-*tert*.-butylbenzyl tetrahydrothiophenium antimony hexafluoride, etc.; anilinium salts such as *N,N*-dimethyl-*N*-benzyl anilinium antimony hexafluoride, *N,N*-dimethyl-*N*-benzyl anilinium boron tetrafluoride, *N,N*-dimethyl-*N*-(4-chlorobenzyl)anilinium antimony hexafluoride, *N,N*-dimethyl-*N*-(*tert*.-phenylethyl) anilinium antimony hexafluoride, etc.; toluidinium salts such as *N*-benzyl-4-dimethylaminopyridium antimony hexafluoride, *N*-benzyl-4-diethylaminopyridium trifluoromethane sulfonic acid, *N,N*-dimethyl-*N*-(4-methoxybenzyl)toluidinium antimony hexafluoride, *N,N*-diethyl-*N*-(4-methoxybenzyl)toluidinium antimony hexafluoride, etc.; phosphonium salts such as ethyltriphenyl phosphonium antimony hexafluoride, tetrabutyl phosphonium antimony hexafluoride, etc.

[0049] Moreover, it is desirable that the compositions of the present invention also contain, in addition to the said vinyl type polymer (P), a crosslinking agent (Q). Blending with the crosslinking agent (Q) will impart excellent weather resistance, reagent resistance solvent resistance and water resistance to the curable resin composition. The

said crosslinking agent (Q) is a compound having more than 2 acid groups in its molecule. There is no specific restriction as to the acid groups. E.g., they include carboxyl group, sulfonyl group, phosphoryl group, etc. Among these groups, carboxyl group is especially desirable.

[0050] The crosslinking agents (Q) include, e.g., acryl compounds obtainable by radical polymerization of a monomer having a carboxyl group that can be represented by such unsaturated monocarboxylic acids as acrylic acid methacrylic acid, cinnamic acid, crotonic acid, etc., and such unsaturated dicarboxylic acids as maleic acid, itaconic acid, fumaric acid, etc., or their monoesters, with other monomers; polyesters having carboxyl groups obtainable by condensation polymerization of unsaturated polybasic acids that can be represented by maleic anhydride, fumaric acid, citraconic acid, itaconic acid, etc., or saturated polybasic acids that can be represented by phthalic anhydride, isophthalic acid, terephthalic acid, orthophthalic acid, naphthalene dicarboxylic acid, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, succinic acid, etc., with polyhydric alcohols that can be represented by ethylene glycol, propylene glycol, 1,3-propane diol, 1,4-butane diol, 1,3-butane diol, 1,5-pentane diol, 1,6-hexane diol glycol, diethylene glycol, triethylene glycol, 1,4-cyclohexane dimethanol, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, etc.; polycarboxylic acids, etc. Among these compounds, polycarboxylic acids are especially suitable.

[0051] The said polycarboxylic acids include, e.g., such aliphatic dibasic acids as adipic acid, sebacic acid, azelaic acid, decane dicarboxylic acid, hexadecane dicarboxylic acid, eicosane dicarboxylic acid, tetraeicosane dicarboxylic acid, etc.; such aromatic polycarboxylic acids as isophthalic acid, trimellitic acid, etc.; such alicyclic dibasic acids as hexahydrophthalic acid, tetrahydrophthalic acid, etc. They can be used individually or as a properly mixed mixture of more than two acids.

[0052] It is desirable that the acid group of the said crosslinking agent (Q) used in the present invention is in the range of 0.5-1.5 equivalents or preferably 0.7-1.3 equivalents or more preferably 0.8-1.2 equivalents with respect to 1 equivalent of the epoxy group and the oxazoline group contained in the said polymerizable monomer (a). It is not desirable that the equivalent ratio of the epoxy group and/or the oxazoline group to the acid group is out of the said range because the degree of crosslinking will decrease and the durability will be lowered.

[0053] In addition to the said vinyl type polymer (P) and crosslinking agent (Q), such curing agents as polyisocyanate compounds, amino plastic resins, etc., may be blended into the curable resin composition of the present invention. Specifically, the said polyisocyanate compounds include, e.g., hexamethylene diisocyanate, tolylene diisocyanate, xylylene diisocyanate, isophorone diisocyanate, derivatives of these diisocyanates, i.e., adduct polyisocyanate compounds, block compounds of polyisocyanates such as cresol block compounds of tolylene diisocyanate, *n*-butanol block compounds of xylylene diisocyanate, etc. They can be used individually or a properly mixed mixture of more than two of these compounds can be used.

[0054] Specifically, the said amino plastic resins include, e.g., methyl etherized melamine resin, butyl etherized melamine resin, butyl etherized benzoguanamine resin, butyl etherized cyclohexyl benzoguanamine, etc. They can be used individually or a properly mixed mixture of more than two of these compounds can be used.

[0055] In addition, an ultraviolet light absorbing agent and/or a hindered amine type stabilizer (HALS) may also be blended into the curable resin composition of the present invention. Blending with the ultraviolet light absorbing agent and/or the hindered amine type stabilizer can further improve the weather resistance of the coated film. The said ultraviolet light absorbing agents include, e.g., such salicylate type ultraviolet light absorbing agents as phenyl salicylate, 4-*tert*.-butylphenyl salicylate, 4-*tert*.-octylphenyl salicylate, etc.; such benzophenone type ultraviolet light absorbing agents as 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid, 2-hydroxy-4-*n*-octoxybenzophenone, 2-hydroxy-4-*n*-dodecyl-oxybenzophenone, 2-hydroxy-4-benzoyloxybenzophenone, bis(5-benzoyl-4-hydroxy-2-methoxyphenyl)methane, 2,2'-dihydroxy-4-methoxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, a mixed product of 2,2'-dihydroxy-4,4'-dimethoxybenzophenone and other 4-substituted benzophenones (e.g., "UVINUL 490", a brand name, manufactured by BASF Co.), 2,2',4,4'-tetrahydroxybenzophenone, 2-hydroxy-4-methoxy-2'-carboxybenzophenone etc; such benzotriazole type ultraviolet light absorbing agents as 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-[2'-hydroxy-3',5'-bis(α,α -dimethylbenzyl)phenyl]-benzotriazole, 2-(2'-hydroxy-3',5'-di-*tert*.-butylphenyl)-benzotriazole, 2-(2'-hydroxy-3',5'-di-*tert*.-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-di-*tert*.-butyl-phenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-di-*tert*.-amyl)benzotriazole, 2-(2'-hydroxy-5'-*tert*.-octylphenyl) benzotriazole, 2,2'-methylenebis [4-(1,1,3,3-tetramethylbutyl)-6-(2*N*-

benzotriazole-2-yl)phenol], etc.; oxalic acid anilide type ultraviolet light absorbing agents, etc. They can be used individually or a properly mixed mixture of more than two of these compounds can be used.

[0056] The said hindered amine type stabilizers include, e.g., bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butane tetracarboxylate, 2,4-dichloro-6-(1,1,3,3-tetramethylamino)-1,3,5-triazine, *N,N'*-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylene diamine polymerization condensation products, etc. They can be used individually or a properly mixed mixture of more than two of these compounds can be used.

10 [0057] The curable resin compositions of the present invention may, if necessary, also contain various additives that are commonly blended into a paint such as an exudation preventing agent, a surface adjusting agent, an antioxidant, a blocking preventing agent, a fluidity adjusting agent, a static controlling agent, a coloring pigment, a curing promoting agent, etc. The curable resin compositions of the present invention show an excellent low temperature curability and also excellent storage stability. Moreover, their solvent resistance, reagent resistance, water resistance, blocking resistance and hardness are also excellent. Therefore, they are very appropriate for use as a paint, a surface treatment agent, a coating agent, a bonding agent, an adhesive, a sealing agent, a forming agent, etc. Especially, when they are used as a paint, they can impart excellent finishing external appearance such as smoothness, sharpness, etc., to the coated film. Therefore, they are quite appropriate for use as a paint for building materials such as aluminum and steel plates, plastics, inorganic materials, etc., and as a paint for automobiles.

20 [0058]

[Actual Examples] Actual examples and comparison examples related to the present invention are described below, but the present invention is by no means limited to these actual examples. Furthermore, the terms "part" and "weight part" used in the actual examples and comparison examples denote "%" and "wt. %", respectively.

30 [0059] Evaluation of the performance characteristics of the coated film of the curable resin composition obtained in the actual examples and comparison examples and the measurements of the physical properties of the vinyl type polymer solution used as the raw material and the crosslinking agent were carried out according to the methods described below.

[Number average molecular weight] Gel permeation chromatography (HCL-8120 GPC, a product of Tosoh Co. Ltd.) was used for the measurement under the conditions given below:

[0060] Elution solution: tetrahydrofuran
Flow rate: 1 mL/minute
Column: TSK gel G5000HXL, GMHXL-L
40 Detection device: differential refractometer

[Glass transition temperature (°C)] A differential scanning calorimeter (DSC-220, a product of Seiko Denshi Kogyo Co. Ltd.) and a rate of temperature rise of 10°C/minute were used in the measurement.

[0061] [Viscosity] Gardner's bubble viscometer was used in the measurement.

[Storage stability] The curable resin composition was stored at 30°C for one month and then its condition was examined by the naked eye. The results were graded as follows:

⊙: excellent, O: good, Δ: fair, X: poor.

50 [Blocking resistance] The curable resin composition was placed in a cylindrical container with a bottom area of about 20 cm² to a height of about 6 cm and was allowed to stand at 30°C for one week. The curable resin composition was then removed and its condition was examined by the naked eye. The results were graded as follows:

[0062] ⊙: no lump, O: some lumps but unbind easily, Δ: lumps present and very difficult to unbind, X: solidified and will not unbind.

[External appearance of coated film] The surface condition of the test plate was examined by the naked eye and was graded as follows:

⊙: excellent, O: good, Δ: fair, X: poor.

[Solvent resistance] The test plate was wrapped 50 times with a cloth wet with methyl ethyl ketone. The surface condition of the test plate was then examined by the naked eye and was graded as follows:

[0063] ⊙: excellent, O: good, Δ: fair, X: poor.

- 10 [Water resistance] The test plate was immersed in warm water at 40°C for one week. Its surface condition was examined by the naked eye and was graded as follows:

⊙: excellent, O: good, Δ: fair, X: poor.

[Acid resistance] One cc of a 40% aqueous sulfuric acid solution was dropped on the coated film surface of the test plate and the test plate was heated for 15 minutes on a hot plate that had been heated to 80°C. The plate was washed with water. The surface condition was then examined by the naked eye and was graded as follows:

[0064] ⊙: excellent, O: good, Δ: fair, X: poor.

- 20 [Weather resistance] A Sunshine Weather Meter (Model "WEL-SUN-HCB" manufactured by Suga Shikenki Co. Ltd.) was used to carry out a progressive weather resistance test on the test plate. The surface condition of the test plate after 2,500 hours of the test was examined by the naked eye and was graded as follows:

⊙: excellent, O: good, Δ: fair, X: poor.

First of all, manufacturing examples of the vinyl type polymer solution, the comparison vinyl type polymer solution and the crosslinking agent are described below.

- 30 [0065] [Manufacturing Example 1 of Vinyl type Polymer Solution] Fifty parts of xylene and 50 parts of butyl acetate as a solvent were placed in a four-mouth flask equipped with a thermometer, a nitrogen gas inlet tube, a dropping funnel and a condenser and the temperature was raised to 100°C. Next, a mixture obtained by mixing 30 parts of glycidyl methacrylate, 1 part of 1,2,2,6,6-pentamethylpiperidiny methacrylate, 50 parts of cyclohexyl methacrylate, 19 parts of butyl acrylate and 2 parts of *tert.*-butylperoxy-2-ethyl hexanoate as a polymerization initiating agent were placed in the dropping funnel. This mixed solution was added drop by drop while stirring under a stream of a nitrogen gas over a period of 2 hours into the solvent that had been heated to 100°C. After the dropwise addition, the mixture was kept at 100°C and stirred for another 4 hours to obtain the vinyl type polymer solution (1). The viscosity of the vinyl type polymer solution (1) thus obtained was Z (viscosity standard solution symbol), the non-vaporizable fraction was 49.8%, the number average molecular weight was 4,500 and the glass transition temperature was 40°C.

- 40 [0066] [Manufacturing Examples 2-7 and Comparison Manufacturing Examples 1-3 of Vinyl type Polymer Solution] Vinyl type polymer solutions (2)-(7) and comparison vinyl type polymer solutions (1)-(3) were prepared according to the procedure used in the Manufacturing Example 1 of the vinyl type polymer solution except that the kinds and the amounts of the polymerizable monomer and the polymerization initiating agent used were changed as shown in Table 1 or Table 2. The viscosity, non-vaporizable fraction, number average molecular weight and glass transition temperature of each vinyl type polymer solution thus obtained are shown in Table 1 and Table 2.

[0067] Symbols given below were used in Table 1 and Table 2.

IPO: 2-isopropenyl-2-oxazoline

50 GMA: glycidyl methacrylate

HALS1: methacryloyloxy-2,2,6,6-tetramethyl piperidine

HALS2: methacryloyloxy-1,2,2,6,6-pentamethyl piperidine

UVA1: 2-[2'-hydroxy-5'-(methacryloyloxyethyl)-2H-benzotriazole

UVA2: 2-[2'-hydroxy-5'-(β-methacryloyloxyethoxy)-3'-*tert.*-butylphenyl]-4-*tert.*-butyl-2H-benzotriazole

CHMA: cyclohexyl methacrylate

MMA: methyl methacrylate

St: styrene

BA: butyl acrylate
 2EHA: 2-ethylhexyl acrylate
 HEMA: 2-hydroxyethyl methacrylate
 MAA: methacrylic acid
 PBO: *tert.*-butylperoxy-2-ethyl hexanoate

[0068]

[Table 1]

		Vinyl type polymer solution						
		(1)	(2)	(3)	(4)	(5)	(6)	(7)
Poly- merizable monomer compo- nent (parts)	IPO	-	-	20	Z	-	40	-
	GMA	30	75	20	15	10	-	30
	HALS1	-	-	-	-	-	-	-
	HALS2	1	0.05	5	-	2	-	1
	UVA1	-	-	10	20	8	8	-
	UVA2	-	-	-	-	-	5	-
	CHMA	50	-	20	35	-	30	-
	MMA	-	15	10	10	32	2	50
	St	-	-	-	-	20	10	-
	BA	10	9.95	-	20	-	-	19
	2EHA	-	-	15	Z	17.9	13	-
	HEMA	-	-	-	-	10	-	-
	MAA	-	-	-	Z	0.1	-	-
Polymerization initiating agent PBO (parts)		2	1	0.5	2	2	1.5	2
Viscosity		Z	Z ₂	Z ₃	Z	Y-Z	Z	Z-Z ₁
Non-vaporizable fraction (%)		49.8	49.9	49.6	50.0	49.8	49.7	49.9
Number-average molecu- lar weight		4,500	6,500	8,000	5,000	4,800	5,500	5,000
Glass transition tempera- ture (°C)		40	40	45	60	55	45	40

[0069]

[Table 2]

		Comparison vinyl type polymer solution		
		Comparison 1	Comparison 2	Comparison 3
Polymerizable monomer component (parts)	IPO	-	-	-
	GMA	30	30	-
	HALS1	-	-	-
	HALS2	-	22	-
	UVA1	-	-	-
	UVA2	-	-	-
	CHMA	50	28	50
	MMA	-	-	15
	St	-	-	-
	BA	20	20	34
	2EHA	-	-	-
	HEMA	-	-	-
	MAA	-	-	-
Polymerization initiating agent PBO (parts)		2	2	2
Viscosity		Y	Z ₂	X-Y
Non-vaporizable fraction (%)		50.1	49.7	50.0
Number-average molecular weight		4,200	4,300	4,500
Glass transition temperature (°C)		35	40	50

[0070] [Manufacturing Example of Crosslinking Agent] Fifty parts of butyl acetate and 50 parts of isopropanol as a solvent were placed in a four-mouth flask equipped with a thermometer, a nitrogen gas inlet tube, a dropping funnel and a condenser and the temperature was raised to 90°C. Next, a mixture obtained by mixing 20 parts of cyclohexyl methacrylate, 30 parts of methyl methacrylate, 20 parts of butyl acrylate, 30 parts of methacrylic acid and 5 parts of 2,2'-azobisisobutyronitrile as a polymerization initiating agent was placed in the dropping funnel. This mixed solution was added drop by drop while stirring under a stream of a nitrogen gas over a period of 2 hours into the solvent that had been heated to 90°C. After the dropwise addition, the mixture was kept at 90°C and stirred for another 4 hours for copolymerization to obtain an acryl resin having carboxyl groups. The non-vaporizable fraction of the acryl resin having carboxyl group was 49.8%, the number average molecular weight was 6,000 and the acid value was 96 mg of KOH per g.

[0071] [Actual Examples 1-7] and [Comparison Examples 1 and 2] The vinyl type polymer solutions (1)-(7) and the comparison vinyl type polymer solutions (1)-(3) obtained from the said manufacturing examples and comparison manufacturing examples of the vinyl type polymer solution and the acryl resin having carboxyl groups obtained from the said manufacturing example of the crosslinking agent were blended in such a way that equivalent quantity of the carboxyl groups contained in the acryl resin per 1 equivalent of the epoxy group and the oxazoline group contained in the vinyl type polymer solution would be the proportions listed in Table 3 to obtain the curable resin compositions (1)-(7) and the comparison curable resin compositions (1) and (2).

[0072]

[Table 3] The curable resin compositions (1)-(7) and the comparison curable resin compositions (1) and (2) thus obtained were spray-coated on a white plate to form a dry film with a thickness of about 25 microns. The white plate used was prepared by coating a zinc phosphate treated steel plate with a two-liquid urethane resin enamel. The coated white plate was then dried at 140°C for 20 minutes for curing to obtain the test plate. This test plate was use to evaluate the performance characteristics of the coated film.

[0073]

[Table 3]

	Actual Example 1	Actual Example 2	Actual Example 3	Actual Example 4	Actual Example 5	Actual Example 6	Actual Example 7	Compara- son Exam- ple 1	Compara- son Ex- ample 2
Vinyl type polymer solution	(1)	(2)	(3)	(4)	(5)	(6)	(7)	Compara- son 1	Compara- son 2
Blending ratio of crosslinking agent *	1.2	0.7	1.0	1.0	1.4	1.0	1.0	1.2	1.2
Per- for- mance char- acter- istics of the coated film	Storage stabili- ty	⊙	○	⊙	⊙	○	⊙	⊙	×
	External ap- pearance of the coated film	⊙	○	⊙	⊙	○	○	⊙	×
	Solvent resis- tance	⊙	⊙	⊙	Δ	○	⊙	×	⊙
	Water resis- tance	⊙	⊙	⊙	○	○	⊙	Δ	×
	Acid resistance	⊙	⊙	⊙	Δ	⊙	○	×	○
	Weather resis- tance	⊙	○	⊙	⊙	○	○	×	⊙

* The equivalent ratio of the carboxyl group with respect to one equivalent of the epoxy group or the oxazoline group.

[0074] [Actual Example 8] and [Comparison Examples 3-5] The vinyl type polymer solution (1) and the comparison vinyl type polymer solutions (1) and (3) obtained from the manufacturing example and the comparison manufacturing example were subject to a reduced pressure distillation process for the removal of the solvent. They were then cooled to obtain the solid vinyl type polymer (1) and the comparison vinyl type polymers (1) and (3). Next, each of the vinyl type polymer and the comparison vinyl type polymers was pulverized and blended with dodecane diacid and a hindered amine stabilizer ("MARKLA-77", a brand name, manufactured by Asahi Denka Kogyo Co. Ltd.). Each of these mixtures was melted and kneaded in a 90°C heat roll. After cooling, the kneaded mixture was pulverized finely in a pulverizing machine and fine particles that had passed through a 150-mesh wire net were collected to obtain the curable resin composition (8) and comparison curable resin compositions (3)-(5).

[0075] The curable resin compositions (8) and the comparison curable resin compositions (3) and (5) thus obtained were coated on a white plate using an electrostatic coating technique to form a dry film with a thickness of about 70 microns. The white plate used was prepared by coating a zinc phosphate treated steel plate with a two-liquid urethane resin enamel. The coated white plate was then dried at 140°C for 20 minutes for curing to obtain the test plate. This test plate was used to evaluate the performance characteristics of the coated film. The results of the evaluation are shown in Table 4.

[0076]

[Table 4]

		Actual Ex- ample 8	Comparison Example 3	Comparison Example 4	Comparison Example 5
Blending ratio (parts)	Vinyl type polymer (1)	100	-	-	-
	Comparison vinyl type polymer (1)	-	100	-	100
	Comparison vinyl type polymer (3)	-	-	100	-
	Dodecane diacid	40	40	40	40
	MARK LA-77	-	-	-	1
Performance characteristics of the coated film	Blocking resistance	◎	◎	x	◎
	External appearance of the coated film	◎	◎	◎	○
	Solvent resistance	◎	x	x	Δ
	Water resistance	◎	Δ	x	Δ
	Acid resistance	◎	x	x	Δ
	Weather resistance	◎	○	x	○

[0077]

[Effects of the Invention] The present invention can provide a curable resin composition that can be cured at a low temperature in a relatively short period of time and that shows excellent storage stability, solvent resistance, reagent resistance, water resistance, blocking resistance, hardness, external appearance with excellent smoothness and especially excellent long-term weather resistance.